

NO REDUCTION WITH CARBON — ANALYSIS OF REACTION MECHANISM BY USING ISOTOPICALLY LABELED NO —

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ABSTRACT

The NO reduction with carbon has been investigated in the presence of oxygen. The use of both mass spectrometer and gas chromatography for gas analysis, together with the use of isotope gas, was quite powerful. It was concluded that N_2 was formed by the reaction between surface nitrogen species and gaseous NO.

INTRODUCTION

Emission of nitrogen oxides is of concern from an environmental point of view as it may be involved in the formation of photochemical smog and acid rain. When they are produced by coal combustion or diesel engines, carbonaceous matter appears to be a good candidate as reducing agent, producing N_2 , CO and CO_2 ^{1,2}. However, oxygen is usually present and particular attention was recently paid to the role it plays in the reduction of nitrogen oxides^{3,4}. These studies clarified the function of oxygen-containing complexes on carbon as reaction intermediates. The presence of nitrogen-containing species at the surface of carbon was also revealed but the species appear to be stable until 1000°C, at least in the absence of oxygen^{2,5}.

The purpose of this study is to investigate the role of nitrogen containing species trapped on the carbon surface in the reduction of NO with carbon in the presence of oxygen.

EXPERIMENTAL

Phenol formaldehyde resin (PF) char is used as carbon source throughout this study. Its preparation was described in details in a recent publication⁴. In a typical experiment, about 200 mg of PF char was placed in a fixed bed reactor under He flow and then heat-treated at 950°C for 30 min immediately before use. The concentration of reactant gas was normally around 500 ppm of NO and 5 % of O_2 both diluted in He. $^{15}N^{18}O$ gas was purchased from Isotec Co. and its isotopic purity is 99 % for N and 95 % for O. Neither isotopically labeled carbon nor O_2 were used in this study.

Gases emitted during experiments are identified and quantified simultaneously by mass spectrometer (MS: Anelva AQA 200) and gas chromatography (GC: Area M200). For GC analysis, MS5 and PPQ columns were used for the separation of O_2 , N_2 and CO and for CO_2 , respectively. Both MS and GC were calibrated by using commercially available standard gases diluted in He.

RESULTS AND DISCUSSION

NO conversion in TPR experiment.

Temperature programmed reactions (TPR) of PF char in the presence of 420 ppm NO were carried out at a rate of 3°C·min⁻¹ (Figure 1). Without O_2 , the reaction began at about 600°C and almost completed at 950°C. In the presence of oxygen (2 vol%), NO conversion started at 200°C but remained lower than 5 % up to 450°C. Thereafter, it increased to be completed at 700°C. Thus, O_2 shifted the conversion curve of NO by more than 200°C. It should be noteworthy that O_2 conversion curve coincided with that of NO. This coincidence was also observed for other carbon samples, brown coal char, activated carbon and graphite, in spite that the reaction started at quite different temperatures for these four carbons. The reaction with O_2 might create reactive sites which are able to react with NO². In the following experiments 600°C was chosen as the reaction temperature, since this is low enough to avoid an excess reaction of NO in the presence of O_2 and high enough to obtain reasonable conversion rate without O_2 .

Reduction of NO at 600°C in the absence of O_2 .

Conversion curve in Figure 1 indicates that NO reduction on PF char is almost negligible at 600°C in the absence of O_2 . However, since pretreatment by oxygen creates reactive sites available for NO reduction, PF char pretreated by 5 % O_2 at 600°C for 20 min was used to react with 530 ppm NO. Figure 2 shows that before introduction of NO into the reactor, only residual evolution of CO was noticed, indicating the desorption of oxygen complexes from the pretreated char. Introduction

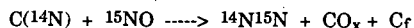
of NO was immediately followed by a dramatic increase of CO production as well as CO₂ and N₂. This indicates the effective reduction of NO even in the absence of O₂. The presence of oxygen-containing sites in char play a key role in this reaction. Thereafter, products concentration decreased to stabilize as NO conversion decreased to a quasi-steady state. After 15 min of the reaction, NO concentration was about 350 ppm in the exhaust gas, corresponding to NO consumption of 180 ppm. N₂ production did not exceed 15 ppm, suggesting the storage of nitrogen species in char. Such compounds are known to be stable, at least under an inert atmosphere to 1000°C^{2,5}.

Reaction of PF char with NO was immediately followed by its TPR at 10°C·min⁻¹ in the presence of 5 % O₂. Figures 3a and 3b show gas evolution during this TPR. The conversion of O₂ started at 500°C (Figure 3a). CO concentration increased first to reach a maximum at 680°C and then decreased while CO₂ reached two maxima at 680 and 830°C and thereafter decreased as the amount of carbon remaining in the reactor became too small. N₂ and NO production profiles were shown in Figure 3b. It seems natural that a part of nitrogen species on PF char, produced in the preceding NO reaction, was oxidized by O₂ and converted to NO. Interestingly, as was reported in the previous paper⁴, the formation of N₂ was observed in spite that only O₂ was present as a reactant. Nitrogen containing surface species was liberated as N₂ with the aid of oxygen. It should be noted that the use of both MS and GC made this observation possible.

Reduction of NO at 600°C in the presence of O₂ — Transient kinetics.

In order to clarify whether N-containing species are involved in NO reduction on PF char or not, the following transient kinetic experiment was done: a mixture of 530 ppm ¹⁴N¹⁶O and 5 % O₂ was flowed through the reactor at 600°C for 21 min and then switched to a flow of 530 ppm ¹⁵N¹⁸O and 5 % O₂ for additional 21 min. The main products were CO and CO₂. First, as shown in Figure 4a, their concentrations increased together with O₂ conversion. This may be related to the activation of PF char. Thereafter, concentrations stabilized and later CO and CO₂ production slowly decreased perhaps because of the loss of carbon. Species produced in lower amounts are presented in Figure 4b. First, the conversion of NO to N₂ increased accompanied with the activation of PF char. NO concentration in this steady state was around 370 ppm, which corresponded to disappearance of about 160 ppm. As N₂ concentration did not exceed 35 ppm, some accumulation of nitrogen in PF char might have taken place during this period.

Switching from ¹⁴N¹⁶O to ¹⁵N¹⁸O resulted in a sudden decrease in ¹⁴N¹⁶O, and various products were formed. Main products were C¹⁶O and C¹⁶O₂ (Figure 4a) with some C¹⁶O¹⁸O (Figure 4b). As nitrogen-containing species, m/e of 29, 30, 31 and 33 were observed and they were assigned to ¹⁴N¹⁵N, ¹⁴N¹⁶O or ¹⁵N₂ (or C¹⁸O), ¹⁵N¹⁶O and ¹⁵N¹⁸O, respectively. The most important observation here is the formation of ¹⁴N¹⁵N. The concentration of ¹⁴N¹⁵N was almost the same as the amount of N₂ determined by GC at least in the initial stage of ¹⁵N¹⁸O/O₂ gasification. This indicates that the main N₂ species was ¹⁴N¹⁵N, and the formation of ¹⁴N₂ (the same m/e with C¹⁶O) and ¹⁵N₂ (the same m/e with C¹⁸O and ¹⁴N¹⁶O) was negligible. In the later stage, however, the discrepancy between ¹⁴N¹⁵N and N₂ (by gas chromatography) became apparent, and therefore ¹⁵N₂ might contribute to some extent in this region. This can be interpreted by the depletion of ¹⁴N-species and accumulation of ¹⁵N-species on carbon. The above observation suggests that the N₂ formation mechanism can be related to the interaction between ¹⁴N-species previously kept in PF char and ¹⁵N¹⁸O in gas phase.



In the previous study¹, it was shown that the possibility of the above mechanism was rather small. However, the previous results were obtained in the absence of oxygen, where the formation rate of N₂ was very low. Moreover, the char was treated for 1 h with He prior to the reaction with NO, and thus the surface nitrogen species was stabilized to some extent. Therefore the present condition is different from that reported earlier and it is more close to the actual gasification condition of interest.

The total NO concentration at 40 min can be expected at around 300 ppm from the extrapolation of the NO concentration between 0 and 21 min, since the reaction itself was continuous before and after gas switching. Unreacted ¹⁵N¹⁸O was 120 ppm and ¹⁵N¹⁶O produced by isotope exchange was 110 ppm. The rest should be ¹⁴N¹⁶O which is the reaction product between surface ¹⁴N and gaseous ¹⁶O₂. Gases for m/e of 46, 30 and 31 evolved rather slowly in the beginning, because accumulation of new surface species by the reaction with ¹⁵N¹⁸O was necessary for the formation of these gases.

CONCLUSION

Use of GC and MS enables to show the gas formation behavior in detail during the NO reduction with carbon in the presence of oxygen. Nitrogen-containing species previously trapped on PF char was removed as either N_2 or NO during TPR in O_2 . The transient kinetic study where $^{14}N^{16}O$ was switched to $^{15}N^{18}O$ in the presence of $^{16}O_2$ clearly showed the formation of $^{14}N^{15}N$. This is a strong evidence for the proposed mechanism of N_2 formation, which involves one nitrogen from surface nitrogen-containing species and another nitrogen from gaseous NO.

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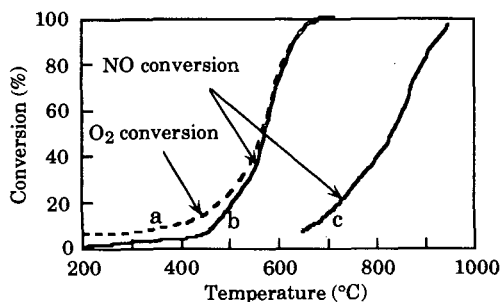


Figure 1 Gas conversion in the presence of PF char.
Reactant gas: (a,b) 420 ppm NO+ 2 % O_2 , (c) 420 ppm NO.

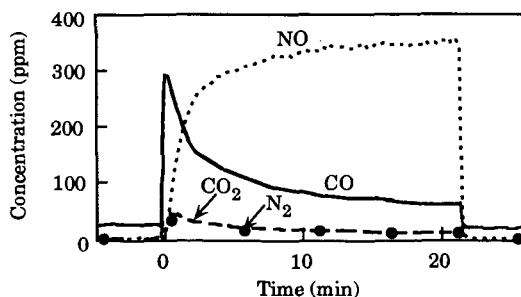


Figure 2 Gas evolution during NO reaction with PF char pretreated with O_2 . Solid marks refer to N_2 concentration determined by GC.

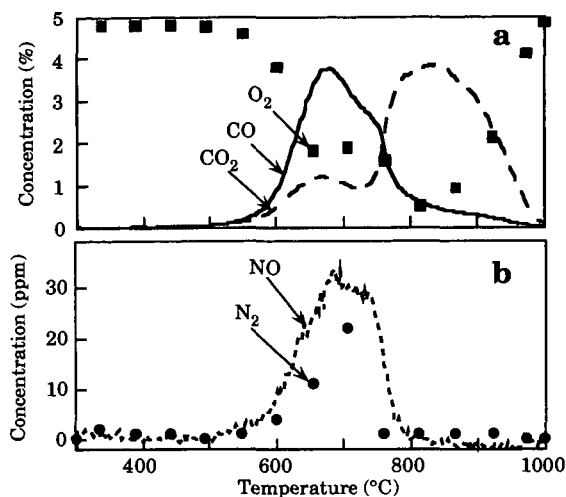


Figure 3 TPR pattern of PF char in the presence of 5 % O_2 . (a) O_2 , CO and CO_2 , (b) NO and N_2 . Solid marks refer to concentration determined by GC.

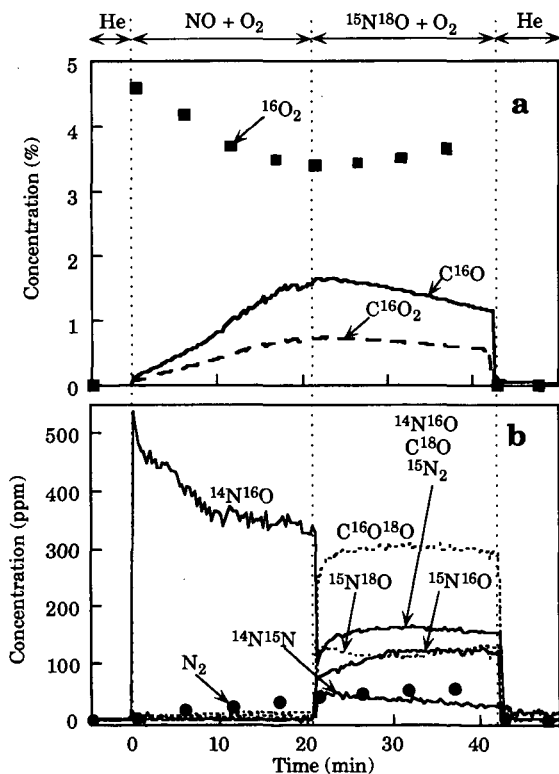


Figure 4 TK pattern on switching from $^{14}N^{16}O$ to $^{15}N^{18}O$ in the presence of 5 % $^{16}O_2$. (a) $^{16}O_2$, $C^{16}O$ and $C^{16}O_2$; (b) N_2 , $^{14}N^{15}N$ and other gases. Solid marks refer to concentration determined by GC.